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(54) **Cast iron alloy for grinding media**

(57) The alloy has the following composition by weight:—

Carbon	4.2% to 6.2%
Silicon	0.2% to 0.8%
Manganese	0.2% to 1.2%
Chromium	15% to 30%
Nickel	0% to 4.0%
Copper	0% to 1.5%
Molybdenum	0% to 0.75%

with the balance being iron and incidental impurities.

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## SPECIFICATION

## Improvements relating to cast iron alloys

- 5 This invention relates to a sand or chill cast iron alloy which finds particular application in the 5  
production of grinding rolls or balls, or tracks therefor, which are used for grinding coal as  
pulverized fuel in the power generation industry. Although the foregoing is a preferred use of  
the alloy of the invention, such a cast iron alloy may also have application in many other  
industries such as cement, ceramic, paint, mining and general metallurgical industries.
- 10 Currently there are many types of mills used for the grinding of coal for use as pulverized fuel 10  
in the power generation industry. However, the most common types all act essentially by rolling  
cast heavy rollers or balls on circular tracks which tracks may be either one-piece or of  
segmented construction. The materials used for the castings are either high-carbon, low-alloy  
steels or alloy white cast irons and it is the latter type which are predominant. Details of such  
15 white cast irons can be found in many National Standards such as for example, BS4844 part 1 15  
to 3 and ASTM A532. These standards cover a wide range of alloys ranging, for example, in  
ASTM A532 from class I type A (3.0% to 3.6% carbon and 1.4% to 4.0% chromium) to class  
III types A (2.3% to 3.0% carbon and 23.0% to 28.0% chromium). Whatever material is used  
there is a continual demand by the industry for an improved abrasion resistance which will give  
20 a longer wear life so that less maintenance and greater mill reliability may be achieved. 20  
Although nickel-chromium irons are still much used (collectively known as Ni-Hard irons), it is  
understood that the high-chromium irons are becoming more popular at present because they  
have a reputation for a greater resistance to premature fracture or breakage. It is well known to  
those working in the power generation industry that, although usually severe impact conditions  
25 are not involved, a measure of fracture resistance is nonetheless as important as wear behaviour 25  
because clearly premature failure would completely negate any improvements that might be  
shown by an alloy in terms of better wear resistance. The main factor affecting wear life is the  
carbide volume fraction or content of the iron since these are much harder than the matrix  
which, depending on the composition and heat treatment of the alloy, may consist of either  
30 tempered martensite or austenite or mixtures of these two together with some bainite. However, 30  
as might be expected, a high carbide content reduces fracture toughness so material selection  
thus becomes a compromise between the various extremes.
- The carbides can be described by the formula  $(\text{Fe, Cr})_3\text{C}_3$  and since carbon is thus a major  
constituent, the carbide volume fraction increases with carbon content. There is a linear  
35 relationship therefore between these two fractions which may be described by the formula:- 35
- $$\% \text{ carbide} = 12.3(\text{C}\%) + 0.55(\text{Cr}\%) - 15.$$
- However, it is very important to realise also that a eutectic occurs in the Fe-Cr-C system  
40 which is also a function of carbon and chromium and, above the eutectic point, hyper-eutectic 40  
massive hexagonal-shaped primary carbides form directly from the melt. In fact, the eutectic  
point can be identified by the following empirical equation:-
- $$\text{E.C.} = 4.4 - 0.054(\text{Cr}\%)$$
- 45 45
- The hyper-eutectic primary carbides are considered undesirable because it has always been  
thought that the fracture and wear resistance of the irons would be impaired by their presence.  
The various aforementioned specifications therefore always dictate that as the chromium in the  
iron is increased, so the carbon content is lowered accordingly.
- 50 The chromium level in the so called high chromium irons ranges from about 11% to 28% 50  
(ASTM-A532) but small percentages of other supplement alloy elements such as molybdenum,  
nickel and copper are used in such irons. These alloying elements are especially necessary when  
an air hardening heat treatment is used because adequate hardenability must be achieved in  
order to form martensitic structures. Apart from carbide content, it may be generally said that  
55 the abrasion resistance increase with increases in hardness and, by such heat treatments, values 55  
of up to 800Hv are achieved. In contrast, some chromium irons are used with a softer austenitic  
matrix and whilst these usually have less than the maximum wear resistance they are better able  
to resist breakage.
- The austenitic high-chromium irons can in some cases work harden on the surface so that  
60 their wear resistance can be stated to be quite good in relation to the original hardness of the 60  
material. Additionally, there is no call to apply costly high temperature hardening heat  
treatment. Again, however, with the need for maximum wear life being paramount, they are not  
so popular as the martensitic irons.
- It is an object of the present invention to provide a cast iron alloy which exhibits the best  
65 possible compromise of all the materials presently available, ie a very good wear resistance, 65

adequate toughness and low cost.

In accordance with the invention there is provided a cast iron alloy having the following composition by weight:-

5	Carbon	4.2% to 6.2%	5
	Silicon	0.2% to 0.8%	
	Manganese	0.2% to 1.2%	
	Chromium	15% to 30%	
	Nickel	0% to 4.0%	
10	Copper	0% to 1.5%	10
	Molybdenum	0% to 0.75%	

with the balance being iron and incidental impurities.

The cast iron alloy defined in the preceding paragraph achieves the object of the invention by using an exceptionally high carbon content in the range 4.2% to 5.2%. As far as is known, this is the highest carbon content ever proposed for a cast ferrous material and this statement could even include alloys that are used for hard facing or welding. For example, Fraser (ASM Technical Report C6-17.2-1966) describes a high-chromium iron which contains only 4.0% carbon and refers to the limited use of even this material.

Hence, pursuant to one aspect of the invention, a carbide level of at least 40% in an austenite matrix results from the alloy, but at the same time, it has been found possible to retain sufficient fracture resistance for those applications in which high impact stresses are not involved, by having an austenitic matrix. Essentially therefore, the adverse effect of the high carbide content is made tolerable or balanced, through the retention of a tough matrix phase. This matrix structure can be achieved through the use of relatively low levels of supplementary alloying elements. Thus, apart from the very high carbon and chromium contents, only a relatively low percentage of the elements nickel, copper, manganese and molybdenum is sufficient to obtain austenite in the as-cast state even in heavy section castings, ie castings having a ruling section of approximately 6 inches because the austenite is saturated with carbon in the as-cast condition. In particular, there is no need to use any substantial amount of molybdenum which, although necessary in the martensitic irons, is extremely expensive. At the same time, the chromium content is used at a high level because this relatively low cost element assists in promoting the desired austenitic matrix.

The alloy of the invention can therefore be used either in the as-cast state or, if the best possible fracture resistance is deemed essential, the alloy may be given a simple low temperature heat treatment.

If the best possible abrasion resistance is required, then, pursuant to another aspect of the invention, the alloy can be heat treated to give an essentially martensitic matrix structure in which case the addition of supplementary alloying elements may have to be somewhat increased. Such an essentially martensitic matrix structure may comprise martensite and approximately 20% austenite having a carbide content of approximately or at least 40%. Such a material will not be quite as fracture resistant or ductile as the austenitic iron referred to in the preceding paragraphs but, suprisingly, it has been found that the effect on ductility is not so marked as might have been supposed. Nevertheless, the use of this particular grade of iron in accordance with the invention must be carefully limited to applications where severe impact is not involved.

Such an iron with a harder essentially martensitic matrix may be produced by giving the as-cast iron a heat treatment for about four hours at 95°C followed by air cooling. Tempering is then preferably carried out at a temperature of approximately 500°C.

By way of a specific example of the alloy of the invention, a cast was made in an electric induction furnace to produce the following alloy wherein the constituent elements are given by percentage weight:-

	Carbon	4.61%	
55	Silicon	0.34%	55
	Manganese	0.40%	
	Sulphur	0.019%	
	Phosphorus	0.025%	
	Chromium	26.86%	
60	Nickel	1.01%	60
	Molybdenum	0.28%	

balance iron and incidental impurities.

A three inch thickness keel or Y-block was poured from the above cast as were a number of round bars suitable for testing by impact, the bars being of three inch length and 0.798 inch

diameter.

A piece taken from one of the bars and also the keel cast as above showed the microstructure of the iron to consist of 57% hyper-eutectic and eutectic carbides in a matrix of austenite. Some of the bars were then tested in an Izod impact test machine in the as-cast state. Others were heat treated at various temperatures and tested to give the results shown in Table 1. Also included in this Table 1, for comparison, are results obtained from a standard NiHard iron of the type that is widely used at present for grinding mill components.

The aforesaid standard Ni-Hard iron referred to in Table 1 had the following constituent elements by percentage weight:-

10	Carbon	3.14%	
	Silicon	0.81%	
	Manganese	0.46%	
	Sulphur	0.077%	
15	Phosphorus	0.062%	15
	Nickel	4.11%	
	Chromium	2.32%	
	Molybdenum	0.20%	

20 balance iron and incidental impurities.

A second melt was made to produce an iron having a carbon content at the maximum upper limit of the invention, this iron having the following analysis by percentage weight:-

	Carbon	5.20%	
25	Silicon	0.58%	25
	Manganese	0.51%	
	Sulphur	0.024%	
	Phosphorus	0.024%	
	Chromium	27.1%	
30	Nickel	0.95%	30
	Molybdenum	0.33%	

balance iron and incidental impurities.

A number of 0.798 inch diameter impact bars were again cast and one of these was examined under the microscope. The structure was found to consist of 65% hyper-eutectic and eutectic carbides in a matrix of austenite. The impact properties and hardness of this iron in various conditions is given in Table 2.

Depending on the conditions it will be seen that the impact resistance of both the iron alloys of the invention were as good or better than that of the Ni-Hard alloy even with a very high carbon and despite the fact that the Ni-Hard was relatively soft and would therefore be expected to exhibit good fracture properties. However, particularly good results were found after an air-cool heat treatment of four hours at 350°C applied to the 4.61% carbon iron.

The wear resistance of the 4.61%C iron alloy of the invention was assessed by using an Amsler pad-on-ring wear tester and again comparing the results to those obtained from a standard Ni-Hard and also to a newly developed iron alloy of the Ni-Hard type. The details of these test results are shown in Table 3.

Although the results of laboratory type wear tests do not always correlate exactly with service performance, this particular Amsler test is known to provide a good guide. Hence, it will be appreciated that the wear life in service can be expected to be very much better than that of either the standard Ni-Hard alloy and better even than the newly developed Ni-Hard type. This does not mean that the alloy of the invention will perform well in every application as may be seen from some wear results using a "grit blast test" which is detailed in Table 4. The poor performance of the iron alloy of the invention in this test is thought due to the fact that the large primary carbide particles have been selectively removed by attack of the softer austenite matrix around them such that they were easily removed.

The standard Ni-Hard iron referred to in Tables 3 and 4 had the following analysis by percentage weight:-

	Carbon	3.20%	
	Silicon	0.62%	
	Manganese	0.66%	
5	Sulphur	0.05%	5
	Phosphorus	0.04%	
	Nickel	3.96%	
	Chromium	2.07%	
	Molybdenum	0.16%	
10	Copper	0.36%	10

balance iron and incidental impurities.

The newly developed iron alloy of the Ni-Hard type referred to in Tables 3 and 4 had the following analysis:-

15			15
	Carbon	3.20%	
	Silicon	1.21%	
	Manganese	0.48%	
	Sulphur	0.06%	
20	Phosphorus	0.57%	20
	Nickel	3.90%	
	Chromium	3.22%	
	Molybdenum	0.77%	
25	Copper	0.29%	25

balance iron and incidental impurities.

However, in situations where rolling abrasive wear is involved, it is expected that excellent results will be achieved. This is because not only will the high volume fraction of carbides provide a distinct advantage but even slight work hardening of the austenite matrix will provide some additional wear resistance. Alloys according to the invention but with carbon contents at the upper end of the specified range would be expected to perform particularly well because, as the data in Table 2 shows, the hardness is dramatically increased.

Subsequent to the laboratory casts as described above, a trial cast was made of a Lopulco type mill roll which is quite a large component having a ring-like shape. The alloy used had the following composition wherein the constituent elements are listed by percentage weight:-

	Carbon	4.73%	
	Silicon	0.66%	
	Manganese	1.20%	
40	Chromium	25.15%	40
	Nickel	2.62%	
	Copper	0.53%	
	Molybdenum	0.55%	

45 balance iron and incidental impurities. 45

The microstructures were found to consist of primary, hyper-eutectic and eutectic carbides in a matrix of austenite together with a slight trace of pearlite. The carbide content was 53% and micro-hardness testing showed this to be 1500Hv. The cast roll was found to be of good general appearance and subsequent ultrasonic testing showed it to be free from any significant porosity or any other casting defects. Since this type of casting is over four feet in diameter and part of the section is over four inches in thickness, this was regarded as a particularly encouraging result in demonstrating the feasibility of manufacturing such items in a satisfactory manner. 50

Thus whilst some alloy white cast irons, although having carbon contents well below those specified herein, have been known to crack whilst cooling in the mold, it is often the accepted solution to this type of problem to lower the carbon content. 55

Referring now to the fully hardened or essentially martensitic grade of iron, an electric furnace melt was made to produce an alloy of the following composition wherein the constituent elements are given by percentage weight:-

	Carbon	6.14%	
	Silicon	0.53%	
	Manganese	0.67%	
5	Chromium	25.34%	5
	Nickel	3.88%	
	Molybdenum	0.19%	

Balance iron and incidental impurities.

- 10 Round bars suitable for testing were produced to 0.798 inch diameter. The micro structure was found to consist of large hexagonal hyper-eutectic and eutectic carbides in a matrix of martensite and approximately 20% austenite; the hardness being 706 Hv30. 10

- Transverse rupture tests using the bars were made on this alloy and compared to the properties obtained from a more conventional 16% chromium iron of the following composition 15
- 15 wherein the constituent elements are given by percentage weight:- 15

	Carbon	3.35%	
	Silicon	0.53%	
	Manganese	0.37%	
20	Sulphur	0.134%	20
	Phosphorous	0.315%	
	Nickel	1.14%	
	Chromium	17.14%	
	Molybdenum	1.58%	
25	Copper	0.05%	25
	Vanadium	0.72%	

balance iron and incidental impurities

The transverse rupture test results are shown in Table 5.

- 30 It will be seen that the strength of the irons of Table 5 was quite similar as was the ductility as measured by the deflection values. Hence, despite accepted opinion, it is possible to use this more wear-resistant alloy in selected applications without a likelihood of premature failure by breakage. 30

TABLE 1  
IMPACT AND HARDNESS RESULTS  
ON A 4.61% C ALLOY

5	10	Material	Condition	Hardness HV30	Individual		5
					Impact Values J	Impact Average J	
15		Iron of the invention	As-cast	586	10.8, 13.5 40.5	21.6	15
20					18.9, 40.5,		20
25			4h/350° A.C.	584	49.9	36.4	25
30					13.5, 16.2,		30
35			4h/650° A.C.	430	47.2,	25.7	35
40		Standard Ni-Hard Iron	16h/275° A.C.	536	16.2, 22.9, 24.3	21.6	40
45					8.1, 16.2,		45
50			4h/550° C A.C. 4h/275° C A.C.	672	40.5	21.6	50
55							55

A.C. = Air Cooled

TABLE 2  
IMPACT AND HARDNESS RESULTS  
ON A 5.2%C ALLOY

5						5
10				<u>Individual</u>		10
				<u>Impact</u>	<u>Impact</u>	
			<u>Hardness</u>	<u>Values</u>	<u>Average</u>	
	<u>Material</u>	<u>Condition</u>	<u>HV30</u>	<u>J</u>	<u>J</u>	
15						15
	Iron			10.8		
	of the			10.8		
20	invention	As-cast	730	13.5	11.7	20
25	Iron			14.8		25
	of the			8.1		
	invention	4h/275°C A.C.	713	13.5	12.1	
30						30
	Iron					
35	of the			16.2,		35
	invention	4h/450°C A.C.	732	17.6	16.9	
40						40
		4h/450°C F.C.				
	Iron	to 275°C.				
45	of the	12h/275°C,		20.2		45
	invention	A.C.	711	27.0	23.6	



TABLE 3AMSLER PAD-ON-RINGWEAR TEST RESULTS

5

5

	<u>Material</u>	<u>Condition</u>	<u>Time on test, h</u>	<u>Wt. Loss Mg.</u>	
10	Iron				10
	of the				
15	invention	As-cast	5	68	15
	Standard				
20	Ni-Hard iron	8h/275°C A.C.	5	161	20
	Improved				
25	Ni-Hard	16h/275°C A.C.	5	100	25

30

30

TABLE 4GRIT BLAST TEST RESULTS

	<u>Material</u>	<u>Condition</u>	<u>Time on test, h</u>	<u>Vol. Loss ccs<sup>3</sup></u>	
35	Iron				35
	of the				
40	invention	As-cast	0.5	825	40
	Standard				
45	Ni-Hard iron	8h/275°C	0.5	307	45
	Improved				
50	Ni-Hard	16h/275°C	0.5	263	50

TABLE 55 TRANSVERSE RUPTURE TEST 5

10 (in accordance with British Standard 1452 Appendix A) 10

15	<u>Material</u>	<u>Heat Treatment</u>	<u>Average Transverse Rupture Strength - N/mm<sup>2</sup></u>	<u>Deflection</u>	15
20	6.14% C -	4h/950°C	437	1.6	20
25	25.34% Cr	Air Cool			25
	Iron of the	6h/500°C			
	Invention	Air Cool			
30	3.35% C -	Ditto	479	1.7	30
	17.14% Cr				
35	Conventional				35
	Iron				

## 40 CLAIMS 40

1. A cast iron alloy having the following composition by weight:-

	Carbon	4.2% to 6.2%		
45	Silicon	0.2% to 0.8%		45
	Manganese	0.2% to 1.2%		
	Chromium	15% to 30%		
	Nickel	0% to 4.0%		
	Copper	0% to 1.5%		
50	Molybdenum	0% to 0.75%		50

with the balance being iron and incidental impurities.

2. A cast iron alloy as claimed in Claim 1 having a carbide content of at least 40% in an austenite matrix.

55 3. A cast iron alloy as claimed in Claim 1 having a carbide content of at least 40% in a substantially martensitic matrix. 55

4. A cast iron alloy substantially as hereinbefore described with reference to the examples.